The search for Nanobubbles by using specular and off-specular Neutron Reflectivity

Philipp Gutfreund* and Marco Maccarini†

Institut Laue-Langevin, 38042 Grenoble, France

Andrew Dennison‡ and Max Wolff

Materials Science, Department of Physics and Astronomy
Uppsala University, 75121 Uppsala, Sweden

April 18, 2013

Abstract

In this work we show an example where specular and off-specular neutron reflectivity can give insight into the structure of solid/liquid interfaces. The presence of nanobubbles and/or a depletion layer at the interface has been long discussed and generated a plethora of controversial scientific results. By means of time of flight neutron reflectometry (NR) and grazing incidence small angle scattering (GISANS), we studied the interface between hydrophobized silicon and heavy water in normal and nigrogen gas enriched state. Our results from the specular reflectivities can be explained without an assumption of a depletion layer and the off-specular measurements show no change with nitrogen super saturated water, which is consistent with the assumption that no nanobubbles are present. We discuss the experiments, in terms of the maximum surface coverage of nanobubbles that could be present on the hydrophobic surface compatible with the limit of sensitivity of NR and GISANS.

1 Introduction

Neutron reflectivity (NR) is one of the major reciprocal space techniques in the structural characterizations of interfaces down to the nanometer scale [1]. More specifically the investigation of buried interfaces, e.g. solid/liquid interfaces, is mainly done by NR or high energy X-rays as those are rarely accessible by soft X-rays or visible light. Neutrons have a further advantage: their particular suitability for soft matter interfaces as cold and thermal neutrons do not radiation damage organic specimens. Furthermore, isotopic substitution offers a powerful

*E-mail: gutfreund@ill.eu
†Present address: CEA, 38054 Grenoble, France
‡Present address: ILL, 38042 Grenoble, France

tool for contrast enhancement of low atomic number elements typically involved in soft matter [2].

Off-specular scattering (OSS), which is typically several orders of magnitude weaker than the specular reflection is not routinely used. This technique has seen most frequent use at synchrotron X-rays sources [1] and in polarized neutron reflectometry [3]. However, recently, the advantage of neutrons in the field of soft condensed matter and the improvements in time-of-flight (TOF) reflectometry have expanded the opportunities to use this technique, due to the higher beam intensities available today [4]. Grazing incident small angle neutron scattering (GISANS) becomes more demanded those days [5] partly due to the unique possibility to use TOF in combination with GISANS to measure depth dependent GISANS patterns in one shot [6].

The solid/water interface constantly attracts interest of fundamental scientists as it is omnipresent in our daily life especially in biological systems [7]. The push for further miniaturization of technology, especially through self-assembly techniques as well as the importance of interfacial phenomena in biological processes highlight the need for further development of our understanding of the physics in these systems. Results of experiments using a model hydrophobic surface at the solid-water interface have proved particularly controversial as a liquid layer of reduced density was observed sandwiched between the hydrophobic surface and the bulk water [8]. In order to quantify the resulting depletion effects, the depletion distance d_2 [9] was introduced:

$$d_2 = \int_{liquid\,phase} (1 - \frac{\rho(z)}{\rho_{bulk}})\, dz, \tag{1}$$

where $\rho(z)$ denotes the density of the depleted liquid at a distance z from the interface and ρ_{bulk} represents the bulk liquid density. d_2 reduces the smeared-out density profile of the depletion to a step-like function that represents an equivalent layer of zero density. The results of NR studies on spin-coated deuterated polystyrene (dPS)/D_2O interfaces showed an apparent depletion distance of $d_2 \approx 2.6\,\text{Å}$ [10], however, a retake of this experiment by another group [11] pointed out that this depletion is not observed when the PS film is freshly prepared and was not exposed to air before the measurement. A similar situation is observed when looking over X-ray reflectivity (XRR) results on bulk water in contact with octadecyl-trichlorosilane (OTS) coated substrates [12] where a depletion distance of only $d_2 = 1.1\,\text{Å}$ was observed and where up to half of the contribution may come from the hydrogen termination of the hydrophobic coating which is practically invisible for X-rays [13]. Thus one can summarize, that if care is taken in order to ensure a clean sample, the resulting depletion between water and hydrophobic surfaces, if present at all, is on a sub-molecular scale and may be due to preferred orientation of water molecules at the interface as suggested by molecular dynamics (MD) simulations [12] or evidenced for organic liquids at hydrophobic surfaces [14, 15, 16, 17].

The situation is more complicated if gas-supersaturated water is used as the exceeding gas may condense in form of a nanoscale layer at a hydrophobic interface [18]. These so-called nanobubbles were initially assumed to be the origin of the hydrophobic gap [10] and raised further reflectivity studies exploiting the influence of different gas enrichments on the water depletion with quite controversial results [19, 20]. A further argument of controversy is the fact that

theoretical calculations predict the lifetime of nanobubbles to be in the μs range [21, 22, 23] and thus not observable in a laboratory time scale. Therefore the observation of nanobubbles has often been attributed to the invasive effect of the Atomic Force Microscopy (AFM) technique [24, 25]. With the introduction of a well established technique to make nanobubbles in a large quantity in the system [26], the so-called solvent exchange technique, it became possible to deliberately produce nanobubbles which are stable on the time scale of hours by replacing ethanol by water. Eventually, nanobubbles were observed with non-invasive techniques like infrared spectroscopy [18] and optical microscopy [27]. Due to their size between 100 - 10000 nm nanobubbles are ideal candidates for investigations with GISANS and specular as well as off-specular NR which is a reciprocal technique and would give an averaged structural result over the whole surface in contrast to the aforementioned microscopy techniques. Previous GISANS measurements [28] on the interface between *d*PS and D_2O were performed on D22 at the Institut Laue-Langevin (ILL) in Grenoble, France but the PS layer was unstable at higher temperatures used to enhance the appearance of nanobubbes. Therefore we decided to use the best established surface to investigate nanoscaled bubbles which is OTS and performed specular and off-specular NR and GISANS on N_2 enriched D_2O in order to get evidence of a depletion layer or nanobubbles.

2 Experimental Details

The silanization of the single crystal silicon (100) block (80*50*20 mm^3, Siltronix, France) was performed according to [29]. The advancing contact angle of *Millipore* filtered water was 102° and the receding one 70°. The specular and off-specular NR measurements, which took 35 min and 10 min, respectively were performed on the FIGARO horizontal sample plane reflectometer at ILL using a wavelength range from 1.7 Å to 19 Å with a relative resolution of $\frac{\Delta\lambda}{\lambda} = 4.2\%$. The reflectivity was measured at two reflection angles (0.625° and 3.2°) with a relative angular resolution of $\frac{\Delta\theta}{\theta} = 3.3\%$. For the GISANS measurements, which were also performed on FIGARO and took 2 h, a wavelength resolution of $\frac{\Delta\lambda}{\lambda} = 7.4\%$ was chosen. The vertical and horizontal angular divergence of the neutron beam was $\Delta\theta_i = 0.02°$ and $\Delta\phi_i = 0.1°$. The detector pixel resolution corresponds to an angular spread of $\Delta\theta_f = 0.018°$ and $\Delta\phi_f = 0.15°$. All resolutions are given as Gaussian equivalent full width at half maximum (FWHM). The solid/liquid sample cell contained about 3 ml of liquid and was mounted with the liquid on top of the solid so that macroscopic bubbles would drift away from the interface under consideration.
The measurement procedure was as follows: Firstly specular and off-specuar reflectivities were recorded on the OTS/D_2O interface by using heavy water as received from *Sigma-Aldrich*, France (99.9 atom % deuteration). Then the water was exchanged by 9 ml of ethanol and after 1 min the ethanol was again exchanged within 100 s by 12 ml D_2O which was saturated with nitrogen by bubbling it with N_2 for 30 min at a temperature of 5 °C. The sample cell and the ethanol were kept at 45 °C throughout the experiment.

Fitting of the reflectivity data was accomplished using co-refinement of a slab model with *Motofit* [30].

3 Results and Discussion

The specular neutron reflectivity (normalized to the Fresnel reflectivity) of the untreated D_2O/OTS interface and of the gas enriched water are plotted in Fig. 1 together with both models assuming and lacking depletion layers. It is not nec-

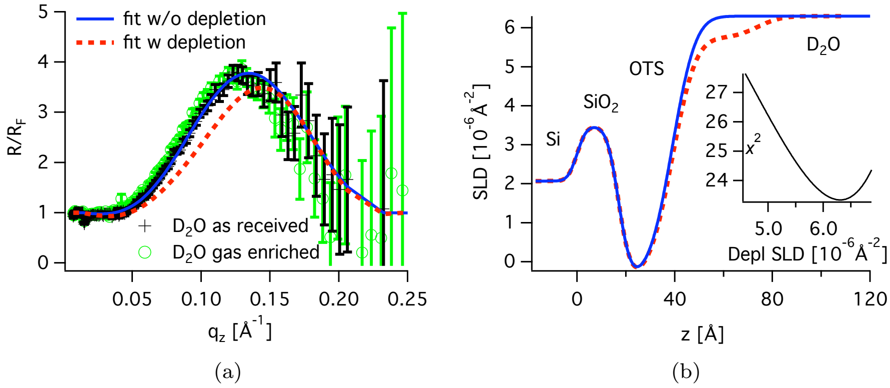
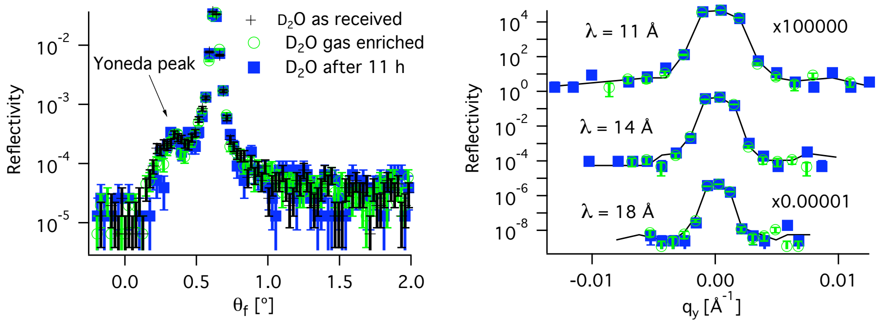


Figure 1: (a) NR normalized to the Fresnel reflectivity for the initial D_2O/OTS interface (black crosses) and the N_2 enriched water (green circles). The best fit without the assumption of a depletion between the OTS and the water is plotted as a solid blue line whereas a depletion layer as observed in [10] would lead to a reflectivity denoted by a red broken line. (b) Scattering length density for the NR fits in the same color code. The inset shows the χ^2 values for different SLDs of the depletion layer.

essary to assume an additional density reduced layer to explain the data. On the contrary, the assumption of an additional density reduced layer sandwiched between the OTS and the water impairs the quality of the fit as can be seen from the χ^2 plot in the inset of Fig. 1(b) where we varied the SLD of a 35 Å thick and 5.5 Å rough depletion layer as it was assumed in [10]. The maximum depletion distance which does not increase the χ^2 more than 5% is $d_2 = 1.9$ Å. This corresponds to a volume fraction of $\sim 2\%$ which would be the maximum volume fraction of nanobubbles in case of a gaseous state. The assumption of a more pronounced depletion as it was observed in [10] leads to a considerably worse fit as can be seen by the broken line in Fig. 1(a).

In Fig. 2(a) we display the off-specular reflectivity curves for the initial interface (black crosses), the gas enriched water immediately after solvent exchange (green circles) and after 11 h (blue rectangles), respectively. The Yoneda peak appears when the exit angle θ_f matches the critical reflection angle of the Si/D_2O interface. As the Yoneda peak intensity originates from an evanescent wave at the interface its intensity is particularly sensitive for in-plane density fluctuations as it would be the case for nanobubbles. Due to the small in-plane momentum transfers in this kind of detector scans the length scale accessible is 1-10 μm. Thus the absence of any influence on gas saturation on the off-specular intensity in Fig. 2(a) means that no bubbles are introduced on the μm scale.

In order to check for smaller bubbles in the range of 50 nm - 400 nm, we performed GISANS, where we should observe a broadening of the reflected peak



(a) (b)

Figure 2: (a) Reflected intensity on a logarithmic scale for detector scans at an incident angle of $\theta_i = 0.625°$ and a wavelength of $\lambda = 5.5$ Å. (b) GISANS intensity cuts (log scale) at the reflected peak for several wavelengths in the same color code. The black line denotes the corresponding direct beams. The results for different wavelengths are shifted vertically for clarity.

in the sample plane or even additional peaks in the q_y scan. In Fig. 2(b) a line cut in y-direction through the specular peak is shown for several wavelengths. No influence of gas saturation on the width of the reflected peak is observed. Moreover the peak width corresponds well to the direct beam which means that it is resolution limited.

4 Summary

In summary, we have shown that with a combination of specular and off-specular reflectivity as well as grazing incidence small angle neutron scattering it is possible to cover a large range of momentum transfers perpendicular and parallel to the surface which play a role in the formation of nanobubbles. Nevertheless, we could not find any evidence on the existence of such nanobubbles even though the well-established technique of solvent exchange was carefully applied. From our present study we conclude that the maximum volume fraction of nanobubbles compatible with our data is $\sim 2\%$. This is much lower than claimed in the cited references and thus we urge the need of surface averaging techniques for further investigations of nanobubbles.

Acknowledgments

We gratefully acknowledge support from the partnership for soft condensed matter (PSCM) at the ILL and financial support by the Swedish research council VR under contract number A0505501.

References

[1] Daillant J and Gibaud A (eds) 2009 *X-ray and Neutron Reflectivity - Principles and Applications* (*Lect. Notes Phys.* vol 770) (Heidelberg: Springer)

[2] Squires G L 1978 *Introduction to the Theory of Thermal Neutron Scattering* (Cambridge: Cambridge University Press)

[3] Zabel H, Theis-Bröhl K and Toperverg B P 2007 *Novel Techniques for Characterizing and Preparing Samples* (*Handbook of Magnetism and Advanced Magnetic Materials* vol 3) (Hoboken: John Wiley & Sons) chap Polarized Neutron Reflectivity and Scattering from Magnetic Nanostructures and Spintronic Materials, p 1237

[4] Jablin M S, Zhernenkov M, Toperverg B P, Dubey M, Smith H L, Vidyasagar A, Toomey R, Hurd A J and Majewski J 2011 *Phys. Rev. Lett.* **106** 138101

[5] Müller-Buschbaum P 2008 *Polymer Surfaces and Interfaces* ed Stamm M (Heidelberg: Springer) pp 17–46

[6] Metwalli E, Moulin J F, Rauscher M, Kaune G, Ruderer M A, Buerck U V, Haese-Seiller M, Kampmann R and Mueller-Buschbaum P 2011 *J. Appl. Crystallogr.* **44** 84–92

[7] Ball P 2003 *Nature* **423** 25–26

[8] Maccarini M 2007 *Biointerphases* **2** MR1–MR15

[9] Mamatkulov S, Khabibullaev P and Netz R 2004 *Langmuir* **20** 4756–4763

[10] Steitz R, Gutberlet T, Hauss T, Klösgen B, Krastev R, Schemmel S, Simonsen A C and Findenegg G H 2003 *Langmuir* **19** 2409–2418

[11] Seo Y S and Satija S 2006 *Langmuir* **22** 7113–7116

[12] Mezger M, Sedlmeier F, Horinek D, Reichert H, Pontoni D and Dosch H 2010 *J. Am. Chem. Soc.* **132** 6735–6741

[13] Ocko B M, Dhinojwala A and Daillant J 2008 *Phys. Rev. Lett.* **101** 039601

[14] Schmatko T, Hervet H and Léger L 2005 *Phys. Rev. Lett.* **94** 244501

[15] Maccarini M, Steitz R, Himmelhaus M, Fick J, Tatur S, Wolff M, Grunze M, Janecek J and Netz R R 2007 *Langmuir* **23** 598–608

[16] Gutfreund P, Wolff M, Maccarini M, Gerth S, Ankner J, Browning J, Halbert C, Wacklin H and Zabel H 2011 *J. Chem. Phys.* **134** 064711

[17] Gutfreund P, Bäumchen O, Fetzer R, van der Grinten D, Maccarini M, Jacobs K, Zabel H and Wolff M 2013 *Phys. Rev. E* **87** 012306

[18] Zhang X H, Khan A and Ducker W A 2007 *Phys. Rev. Lett.* **98** 136101

[19] Doshi D A, Watkins E B, Israelachvili J N and Majewski J 2005 *PNAS* **102** 9458–9462

[20] Mezger M, Reichert H, Schöder S, Okasinski J, Schröder H, Dosch H, Palms D, Ralston J and Honkimäki V 2006 *Proc. Natl. Acad. Sci.* **103** 18401–18404

[21] Attard P 2003 *Adv. Coll. Int. Sci.* **104** 75

[22] Brenner M P and Lohse D 2008 *Phys. Rev. Lett.* **101** 214505

[23] Colaco R 2009 *Surface Science* **603** 2870

[24] Ishida N 2000 *Langmuir* **16** 6377

[25] Tyrrell J W G and Attard P 2001 *Phys. Rev. Lett.* **87** 176104

[26] Lou S, Gao J, Xiao X, Li X, Li G, Zhang Y, Li M, Sun J and Hu J 2001 *Chin. Phys.* **10** S108–S110

[27] Karpitschka S, Dietrich E, Seddon J R T, Zandvliet H J W, Lohse D and Riegler H 2012 *Phys. Rev. Lett.* **109** 066102

[28] Steitz R 2004 Experimental Report 9-11-1016 ILL

[29] Wang Y and Lieberman M 2003 *Langmuir* **19** 1159–1167

[30] Nelson A 2006 *J. Appl. Crystallogr.* **39** 273–276